



Effect of sulphur on the performance of Rh–LaCoO₃ based catalyst for tar conversion to syngas

P. Ammendola, E. Cammisa, R. Chirone, L. Lisi*, G. Ruoppolo

Istituto di Ricerche sulla Combustione CNR – P.le Tecchio, 80 – 80125 Naples, Italy

ARTICLE INFO

Article history:

Available online 29 July 2011

Keywords:

Rh catalysts
Perovskite
Sulphur-poisoning
Biomass
Tar

ABSTRACT

The effect of sulphur addition on the catalytic activity of 1%Rh/Al₂O₃, LaCoO₃/Al₂O₃ and 1%Rh–LaCoO₃/Al₂O₃ catalysts in reforming of tar produced by biomass pyrolysis has been investigated by adding 20 or 200 ppm H₂S in a fixed bed reactor at 700 °C using a S-free biomass slowly pyrolyzed. The catalysts have been characterized by ICP-MS and BET analyses. The poisoning effect of sulphur has been also studied by in situ DRIFT and TPR analyses. A very high sulphur exposure of the catalysts leads to the partial inhibition of the reforming properties related to the poisoning of dispersed rhodium sites. The LaCoO₃ layer effectively preserves rhodium from sulphur poisoning in the 1%Rh–LaCoO₃/Al₂O₃, the catalyst containing both phases showing mostly unchanged catalytic properties also upon 200 ppm S-treatment under reaction conditions. The LaCoO₃/Al₂O₃ catalyst shows reduced reforming properties coupled to an increase of cracking and total oxidation reactions associated to the partial destruction of the perovskite structure.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Biomass is attracting an increasing interest in the last years as possible renewable fuel. Its gasification is a developing technology to produce syngas that can be used in gas turbines, fuel cells or Fischer–Tropsch synthesis.

The gas fraction can be enhanced by fast heat transfer, high temperatures and presence of an oxidizing agent. Nevertheless, the formation of tar represents a severe limitation and its conversion is required [1]. Catalytic tar conversion can further increase the whole gas yield promoting reforming of hydrocarbons in the gas lowering the operating temperature at the same time. The use of dolomite or Ni based catalysts was proposed as in-bed or secondary catalysts, respectively [2]. In a previous paper a Rh–LaCoO₃ based catalyst was proposed by the authors for the conversion of tar produced by thermal decomposition of biomass into syngas [3]. Its performance was investigated in a double fixed bed reactor, suitably designed to test the catalyst in direct contact with biomass devolatilization products [4]. The novel catalyst completely converted tar and light hydrocarbons into syngas with a limited coke formation whereas, under the same conditions conventional materials (dolomite, olivine and Ni/Al₂O₃ catalysts) left a fraction of unconverted tar and produced a gas containing large amounts of hydrocarbons and CO₂ [4].

Nevertheless, biomasses as straw, cereals, grasses and fruit residues contain not negligible amounts of S, N and Cl [5] which can hinder the catalyst activity, especially affecting the noble metal properties.

Sulphur strongly reduces the reforming activity of traditional Ni-based catalysts by chemisorbing on Ni sites [6]. Nickel sulphide is generally formed under reducing conditions [7] whereas in the presence of O₂ oxidation of H₂S and consequent formation of NiSO₄ can occur [6]. On the contrary, sulphur has a positive effect at low temperature (600–700 °C) on naphthalene and ammonia decomposition for ZrO₂ and Y₂O₃–ZrO₂ with an intensity increasing with the Lewis basicity of the material [8].

Sato and Fujimoto [9] reported that WO₃ addition to a Ni/MgO–CaO catalyst improves the resistance to sulphur and coking by promoting the formation of WS_x from NiS, tungsten being then regenerated by H₂. Deactivated Ni-based catalysts can be regenerated at high temperature under reducing conditions but the process requires a long time and a large volume of sulphur-free gas although alternative more effective regeneration processes was recently proposed [6].

A more stable activity in the presence of H₂S was found by Tomishige et al. [10] for a Rh/CeO₂/SiO₂ catalyst compared to Ni-based systems attributed to a lower sulphur adsorption related to a surface cleaning occurring in the fluidized bed reactor used for the partial oxidation of tar.

On the other hand, Rh based catalysts can be significantly deactivated by sulphur which mainly affects the steam-reforming properties of the noble metal in the partial oxidation of methane

* Corresponding author.

E-mail address: lisi@irc.cnr.it (L. Lisi).

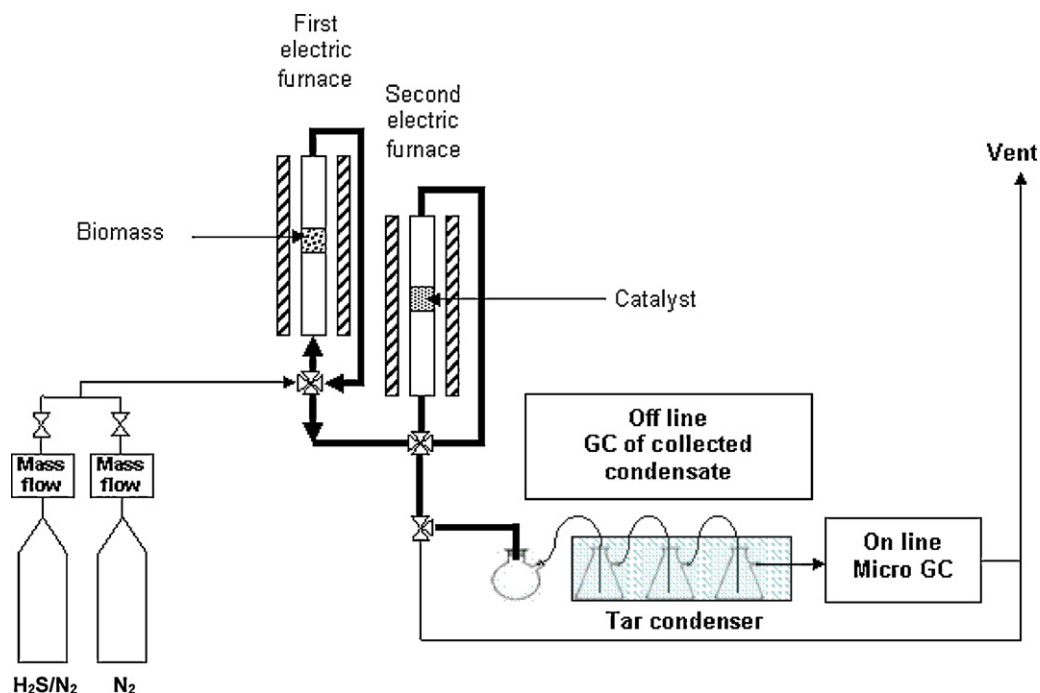


Fig. 1. Scheme of the catalytic test plant.

[11,12], although at quite low temperature (800 °C) alumina support acts as a buffer adsorbing sulphur and preventing deactivation for a long time [12].

Deactivation by sulphur of perovskite-based catalysts was extensively studied under oxidative conditions (combustion) [13–16]. Basic properties of lanthanum were supposed to promote SO₂ adsorption with consequent formation of lanthanum sulphate and sulphite and metal oxide from the B cation which irreversibly causes the destruction of the perovskite structure [15,17]. Morphological changes upon sulphur poisoning were also observed for structured perovskite-based catalysts [14]. Nevertheless, no studies are available about the effect of sulphur compounds under reducing conditions.

In this paper, an alumina supported Rh–LaCoO₃ has been studied for catalytic tar conversion in the presence of sulphur and its performance compared with that in the absence of this poisoning agents. An in situ DRIFT investigation and a TPR analysis of poisoned catalysts have been coupled to the activity tests in order to characterize the active sites and understand the poisoning effect of sulphur. The role played by perovskite and noble metal in the poisoning process has also been investigated on catalysts containing the single phases (LaCoO₃ or Rh).

2. Experimental

2.1. Biomass

Maple wood chips were used as biomass with the following composition: moisture (8.9 wt%), volatiles (74.6 wt%), fixed carbon (15.9 wt%) and ash (0.6 wt%) [3]. The chemical composition, estimated on dry basis is: 46.28 wt% C, 5.56 wt% H, 47.52 wt% O, 0 wt% N, 0 wt% S, estimated using both a CHN2000 (LECO) and a SC-144DR (LECO) analyzer.

2.2. Catalysts preparation

The Rh (0.5–1 wt%) promoted LaCoO₃ (20 wt%) supported on La stabilized γ -Al₂O₃ catalysts were prepared by wet impregnation of

a commercial La₂O₃ (3 wt%) stabilized alumina (Puralox SCF140-L3 Sasol) with suitable amounts of Rh(NO₃)₃·xH₂O (Riedel-de-Haën), La(NO₃)₃·xH₂O (Aldrich, >99.9%) and Co(NO₃)₂·6H₂O (Fluka, ≥99%), as described in [3]. Two samples containing rhodium (1 wt%) only and LaCoO₃ (20 wt%) only were also prepared using the same support.

All catalysts were dried at 120 °C and calcined at 800 °C (heating rate: 10 °C min⁻¹) for 3 h in flowing air (150 ml min⁻¹).

2.3. Catalysts characterization

Chemical composition of different samples was determined with an ICP-MS Agilent 7500 instrument. Surface area was measured by N₂ adsorption at 77K (BET method) with a Quantachrome Autosorb 1-C analyzer.

H₂ TPR experiments were carried out with a Micromeritics Autochem II TPD/TPR analyzer reducing about 100 mg catalyst with a 2% H₂/Ar mixture (50 N cm³ min⁻¹) at 10 °C min⁻¹ up to 800 °C. The fresh catalysts were pre-treated 1 h in air (50 N cm³ min⁻¹) at 800 °C before the experiment. The S-poisoned catalysts were pre-treated with 200 ppm H₂S/N₂ mixture at 700 °C for 2.7 h (typical time length of the catalytic test after described later on) using the same contact time of catalytic activity tests. For fresh catalysts a cold trap was used to keep water before TCD whereas for poisoned catalysts a KOH based trap was used in order to keep also H₂S, H₂SO₄ or H₂SO₃ possibly produced by the reaction between hydrogen and sulphide, sulphate or sulphite compounds.

DRIFTS experiments were performed on 1%Rh–LaCoO₃/Al₂O₃ with a Perkin Elmer Spectrum GX spectrometer equipped with a high-temperature Pike DRIFT cell with a ZnSe window connected to mass flow controlled gas lines. Spectra were averaged over 50 scans with a spectral resolution of 4 cm⁻¹. The poisoning of Rh species was investigated using CO as a probe molecule. Prior to the experiment the sample was reduced with a 2% H₂/N₂ mixture for 1 h at 800 °C and then cooled down to room temperature under the same mixture. After 15 min Ar purging a background spectrum was recorded; then CO was adsorbed at room temperature (2% CO/N₂ mixture, 100 N cm³ min⁻¹) for 30 min and any excess

CO was removed by flushing with Ar ($100 \text{ N cm}^3 \text{ min}^{-1}$) prior to recording the DRIFT spectrum. In another experiment the catalyst was poisoned in situ with 20 ppm H_2S in H_2/N_2 mixture for 15 min and 120 min at 700°C and then, after Ar purging, CO was adsorbed at room temperature.

2.4. Catalytic tests

A scheme of the experimental rig for catalytic tests in the presence or in the absence of sulphur in the feed is shown in Fig. 1. Two fixed bed quartz reactors in two different electric furnaces were used to heat independently the biomass and the catalyst as described in [3]. The dried biomass (500 mg) was heated at 5°C min^{-1} up to 800°C in the first furnace under N_2 (12 N l h^{-1}). The gaseous and condensable products produced passed through the second reactor containing the catalyst (500 mg) at 700°C . Unconverted tars were collected in a two stage-condenser downstream the second reactor following the CEN/TS 15439 (2006) procedure [18]. The lines connecting the reactors and the tar condensation train were heated ($300\text{--}400^\circ\text{C}$) to avoid the condensation of tarry compounds. The permanent gases were analyzed with a microGC (Agilent 3000A). The residual solid material in the first reactor was weighted to determine the char yield. The sampling train was weighted before and after the experiment for the quantitative evaluation of the condensable tars yield. The analysis of the condensed tars was performed off line in a gas chromatograph (HP 9600 series) after diluting with isopropanol. At the end of each experiment the amount of coke deposited on the catalyst was determined by oxidation evaluating the amount of released CO_2 . The oxidation was performed following a heating ramp of 5°C min^{-1} from room temperature up to 800°C under a $0.5\% \text{ O}_2/\text{He}$ mixture constant flow rate (17 N l h^{-1}).

In the catalytic tests in the presence of sulphur a 20 or 200 ppm $\text{H}_2\text{S}/\text{N}_2$ gas mixture (12 N l h^{-1}) was fed to the first reactor. Due to the special plant configuration, the length of the catalytic tests cannot be modified being related to the biomass devolatilization occurring at 5°C min^{-1} , as a consequence a longer exposition of the catalyst to a S-containing feed was simulated using a higher H_2S concentration (200 ppm rather than 20 ppm). In the tests in the presence of H_2S both gaseous and condensable compounds were also analyzed using a Hewlett Packard G1540A gas-chromatograph equipped with a FID for the analysis of organics and an Agilent Dual Plasma 355 Sulphur Chemiluminescence detector for the analysis of S-containing species. To this aim gaseous products were collected in tedlar gas sampling bags every 40 min and injected in the GC. Before catalytic tests a blank run was carried out excluding the first reactor and the quantitative and qualitative analysis of the

Table 1

Metal concentration and specific surface areas of catalysts.

Catalyst	Rh content (wt%)	Co content (wt%)	Surface area (BET) ($\text{m}^2 \text{ g}^{-1}$)
1%Rh/ Al_2O_3	0.84	–	134
LaCoO ₃ / Al_2O_3	–	4.70	101
1%Rh–LaCoO ₃ / Al_2O_3	0.80	4.72	104
0.5%Rh–LaCoO ₃ / Al_2O_3	0.45	4.50	99

biomass pyrolysis products under $\text{H}_2\text{S}/\text{N}_2$ flow was done. Sulphur concentration in the residual char was determined with a SC-144DR (LECO) analyzer.

Possible catalytic activity changes due to the presence of sulphur in the feed were estimated as the difference between the yields and type of gas, liquid and solid products obtained between the tests with and without sulphur feeding. For all experiments the mass balance was closed with a maximum error of $\pm 10 \text{ wt}\%$.

3. Results and discussion

3.1. ICP, BET and XRD characterization of fresh catalysts

The catalysts properties are summarized in Table 1. The catalysts showed high specific surface areas, thanks to the use of $\gamma\text{-Al}_2\text{O}_3$ used as support, which has a surface area of $140 \text{ m}^2 \text{ g}^{-1}$. As expected, the superficial area decreased with increasing the active phase loading, i.e. superficial area was minimized when 20 wt% of LaCoO₃ was deposited, the very small amounts of rhodium did not further affect that value. The perovskite based catalysts contained cobalt in amounts close to the nominal one (4.8 wt%). Rhodium was present in lower amounts than the expected nominal ones (1 and 0.5 wt%), due to an undefined hydration of the Rh nitrate precursor.

3.2. Catalytic tests

The pyrolysis products of the maple wood chips used as biomass were mainly constituted of gaseous species such as CO, CO_2 , H_2 and light hydrocarbons (7.8 wt%), condensable hydrocarbons (74.6 wt%) and char (16.6 wt%). This distribution was not significantly affected by the H_2S addition, as shown in Table 2. Therefore, the pyrolysis products passing through the catalytic bed in the second reactor can be considered the same in the absence or in the presence of H_2S and, as a consequence, the different activity of the catalyst should be ascribable to the poisoning effect of sulphur only and not to a different concentration and type of reagents. GC analysis of sulphur products carried out during the

Table 2

Solid, liquid and gas yields on dry basis obtained during the reaction tests.

Catalyst	H_2S concentration in the feed (ppm)	Solid yield (wt%)		Tar yield (wt%)	Gas yield (wt%)
		Char	Coke		
–	0	16.6	–	74.6	7.8
	20	18.1	–	75.8	7.3
LaCoO ₃ / Al_2O_3	0	18.3	3.5	–	75.9
	20	17.6	5.5	7.9	59.0
1%Rh/ Al_2O_3	0	16.5	2.0	–	76.5
	20	17.7	2.0	–	75.1
	200	18.5	5.1	3.7	64.3
1%Rh–LaCoO ₃ / Al_2O_3	0	18.0	1.1	–	77.6
	20	16.8	2.4	–	75.0
	200	18.1	3.0	–	69.5
0.5%Rh–LaCoO ₃ / Al_2O_3	0	17.6	1.7	–	70.7
	20	18.1	3.0	–	69.1

Table 3
Light hydrocarbons (μmol) detected in the gas phase.

Catalyst	H ₂ S concentration in the feed (ppm)	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆ /C ₃ H ₈	nC ₄	nC ₅	1-Pentene	1-Hexene
–	0	0	0.7	0.6	0	1.1	0.2	1.3	1.6
	20	0	0	0	0	0.7	0.7	8.6	0
LaCoO ₃ /Al ₂ O ₃	0	0	2.1	2.8	0	0	0	0	0
	20	0	414	54.3	88.4	0	0	0	0
1%Rh/Al ₂ O ₃	0	0	0	0	0	0	0	0	0
	20	0	0	0	0	0	0	0	0
	200	0	159	0	9.7	1.5	0	0	0
1%Rh–LaCoO ₃ /Al ₂ O ₃	0	0	0	0	0	0	0	0	0
	20	0	0	0	0	0	0	0	0
	200	0	142	0	16	3	0	0	0
0.5%Rh–LaCoO ₃ /Al ₂ O ₃	0	0	0	0	0	0	0	0	0
	20	0	28.6	7.28	0	0	0	0	0

biomass decomposition at different times showed that no other S-containing compounds but H₂S are present in the outlet gas stream. The H₂S concentration remained the original one up to 550 °C, then it starts to decrease corresponding to the formation of high surface area char, able to adsorb H₂S. As matter of fact, sulphur was found in the residual char in concentration consistent with that of H₂S missing in the outlet stream at temperature higher than 550 °C. All these results are an indication that H₂S is not involved in the biomass pyrolysis confirming that the decomposition takes place according to the same mechanism in the absence or in the presence of sulphur and that some sulphur is trapped in char at high temperature.

In Table 2 the performance of the catalysts is reported as solid, liquid and gas yields in the presence or in the absence of sulphur.

In all catalytic experiments the char yield is in the range 16.5–18.5 wt%, as expected from the preliminary blank runs of biomass pyrolysis.

In the stream exiting the second reactor after the condensation train only H₂S was detected and no formation of SO₂ or COS nor of other thio-compounds were observed. For both H₂S inlet concentrations the H₂S fraction in the outlet gas decreased due to the contribution of both catalyst poisoning and char adsorption, the latter starting from a biomass decomposition temperature of about 550 °C, as confirmed by blank tests carried out on biomass. In particular, for the H₂S inlet concentration of 20 ppm no H₂S was found in the outlet stream from 550 °C, whereas 30–40 ppm of H₂S were still present in the outlet gas in the high temperature region of biomass decomposition for the 200 ppm H₂S inlet feed.

All Rh containing catalysts completely convert tar also in the presence of 20 ppm H₂S, keeping quite unchanged the gas yield. Otherwise, a significant poisoning effect of sulphur was observed for LaCoO₃/Al₂O₃ catalyst which shows a lower gas yield associated to a lower tar conversion and a larger coke formation. Nevertheless, as general trend, a slight reduction of gas yield balanced by an

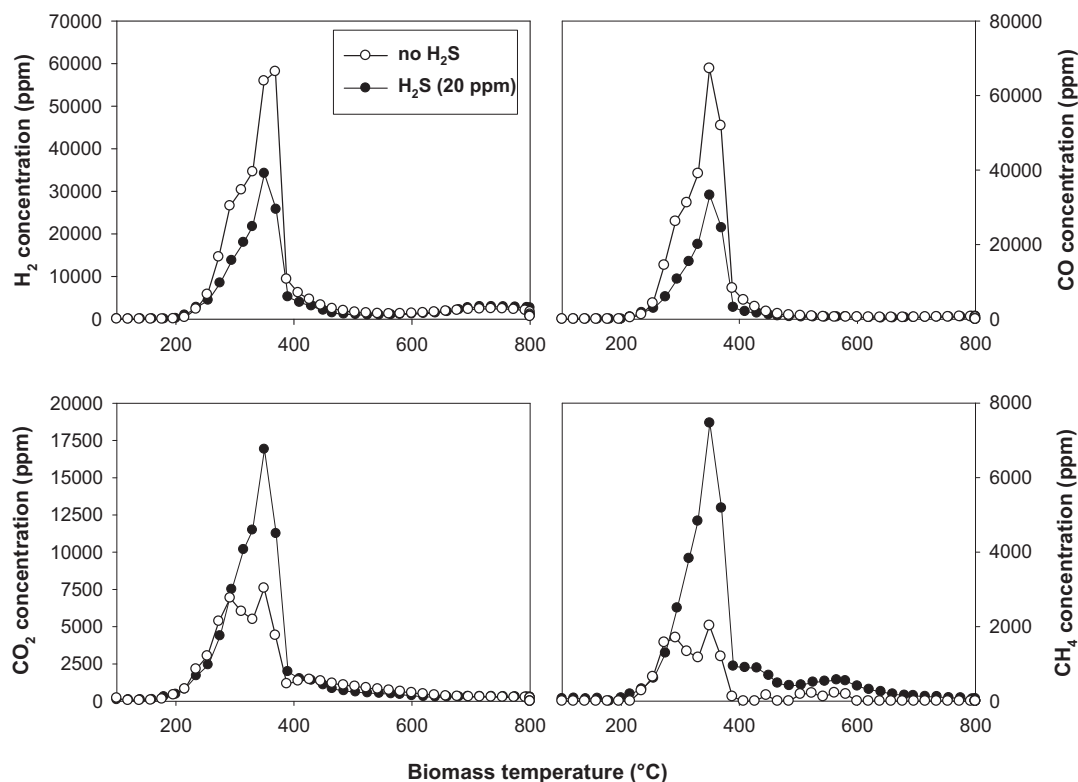


Fig. 2. H₂, CO, CO₂ and CH₄ concentration profiles as functions of biomass decomposition temperature obtained on LaCoO₃/Al₂O₃ under different H₂S concentrations.

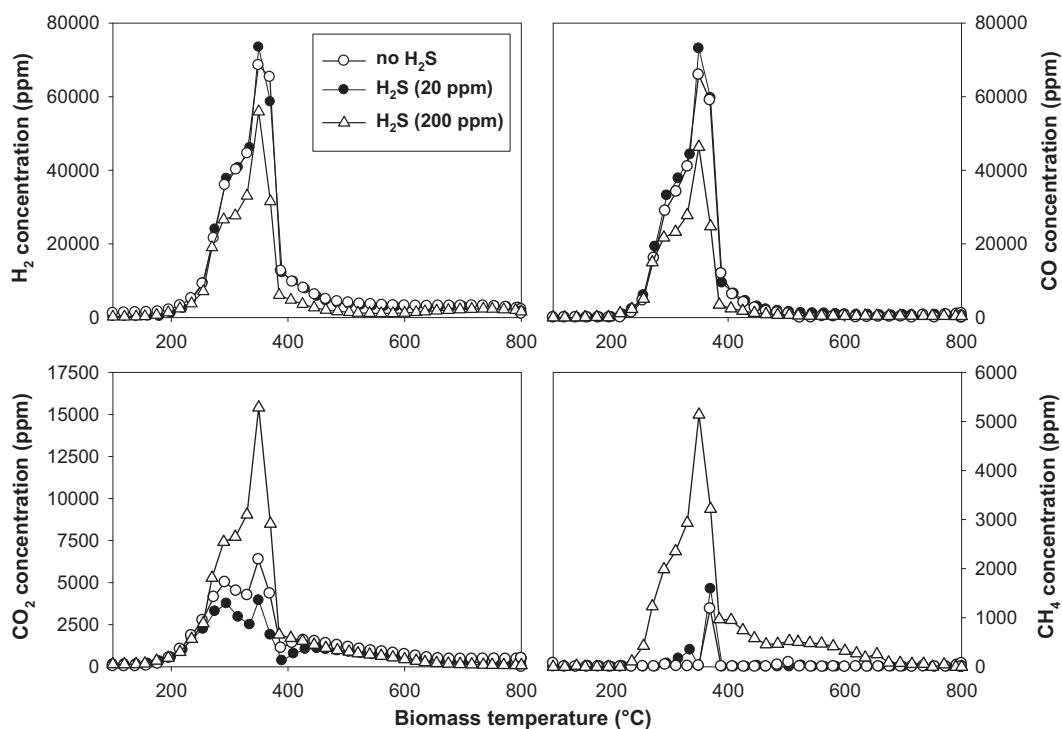


Fig. 3. H₂, CO, CO₂ and CH₄ concentration profiles as functions of biomass decomposition temperature obtained on 1%Rh/Al₂O₃ under different H₂S concentrations.

increased coke deposition was observed in the presence of sulphur for all catalysts.

In Fig. 2 the H₂, CO, CO₂ and CH₄ profiles evaluated in the catalytic tests in the absence and in the presence of sulphur are compared for the LaCoO₃/Al₂O₃ catalyst. The analysis of the gas phase for this sample reveals that, in addition to a general activ-

ity loss, the reforming properties are those mainly influenced by the presence of H₂S. The amount of H₂ and CO produced by tar conversion is strongly decreased and, at the same time, the concentration of total oxidation and cracking products (CO₂ and CH₄, respectively) increases. The increased formation of unconverted light hydrocarbons was also associated to the reduction of the

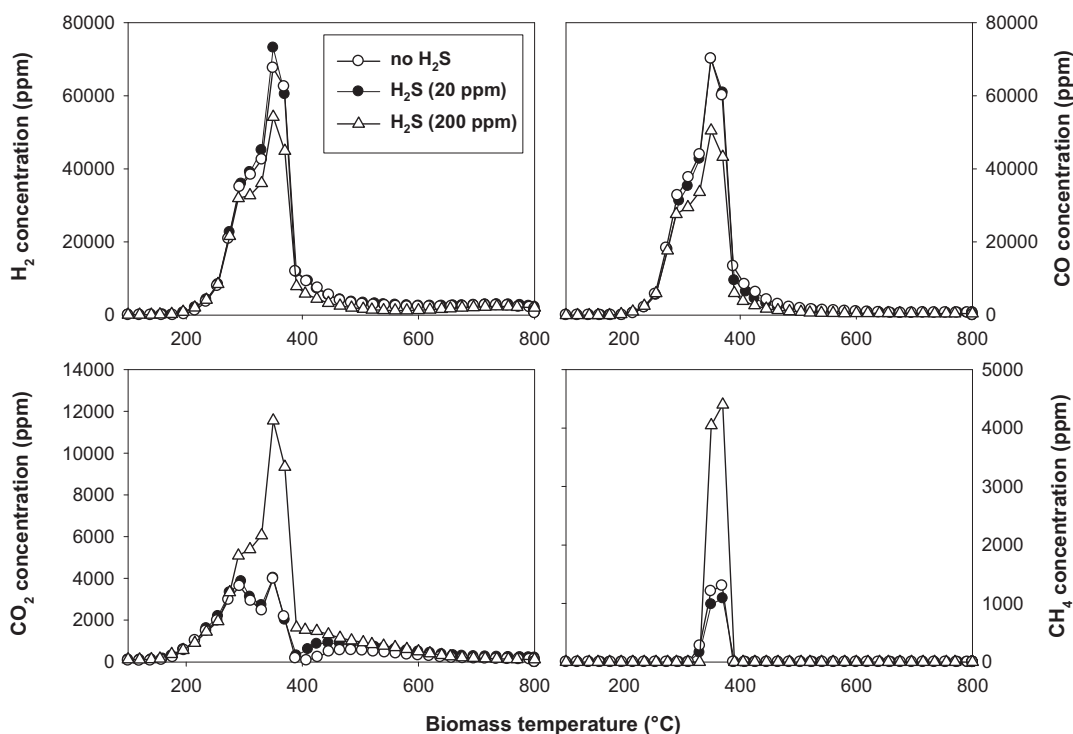


Fig. 4. H₂, CO, CO₂ and CH₄ concentration profiles as functions of biomass decomposition temperature obtained on 1%Rh-LaCoO₃/Al₂O₃ under different H₂S concentrations.

reforming properties, as shown in Table 3. Indeed, these species are produced by cracking reactions promoted by the catalysts and are not converted due to the poisoning of reforming sites.

For Rh containing catalysts, in Figs. 3 and 4 the comparison of H_2 , CO, CO_2 and CH_4 profiles obtained in the absence and in the presence of the low sulphur concentration for 1%Rh/ Al_2O_3 and 1%Rh-LaCoO₃/ Al_2O_3 catalysts is reported in order to show the overlapping of the corresponding curves. The presence of light hydrocarbons, different from methane, was not observed also with 20 ppm of H_2S in the feed (Table 3). The analysis of the gas phase of 0.5%Rh-LaCoO₃/ Al_2O_3 , not reported, reveals a slight decrease of H_2 and CO, accompanied with an increase of CO_2 , CH_4 and light hydrocarbons (Table 3).

These results thus indicate that the perovskite layer preferentially could adsorb sulphur preserving the noble metal from this poisoning agent at least for low H_2S concentration. Therefore, Rh sites can be still available for tar and light hydrocarbons reforming until cobalt and lanthanum adsorb sulphur. When the perovskite is not present in the catalyst formulation the alumina surface can have a similar protection effect.

The two most performing catalysts, 1%Rh/ Al_2O_3 and 1%Rh-LaCoO₃/ Al_2O_3 , were tested under more severe poisoning conditions (200 ppm H_2S). As already mentioned before, due to the fixed length of the experiment related to the biomass decomposition under a programmed heating rate, it would be impossible to produce a long exposure of the catalyst to sulphur. Thus, that was simulated by dramatically increasing the sulphur concentration in the feed. The results are also reported in Tables 2 and 3.

When the 1%Rh/ Al_2O_3 catalyst is exposed to 200 ppm H_2S some unconverted tar was found and, at the same time, the coke deposition significantly increases to the detriment of gas phase (Table 2). Together with the appearance of some unconverted hydrocarbons in the gas phase (Table 3), the H_2 and CO concentration decreases, whereas the CO_2 and CH_4 ones increases (Fig. 2). Thus the alumina surface starts to be saturated at much higher sulphur concentration and its buffer role starts to finish and poisoning of active Rh sites begins. The performance of 1%Rh-LaCoO₃/ Al_2O_3 is also affected by the presence of H_2S in high concentration, even if in a less extent than 1%Rh/ Al_2O_3 . In particular no tar was detected also under this conditions. These results show that the Rh-based catalyst with the perovskite layer covering the alumina surface should have a higher saturation level.

The negative effect of sulphur on steam-reforming reaction rather than on oxidation reactions was also reported by Ferrandon et al. [20] who supposed that sulphur inhibits carbon-steam reactions as well to explain the increased coke formation they found for a Rh/La- Al_2O_3 catalyst in gasoline reforming.

3.3. DRIFT and TPR characterization of fresh and poisoned catalysts

Poisoning of Rh sites promoting the reforming reactions was confirmed by the DRIFT experiments.

Before the experiment on 1%Rh-LaCoO₃/ Al_2O_3 catalyst, a spectrum of CO adsorbed on a pre-reduced LaCoO₃/ Al_2O_3 catalyst was taken. Signals in the region of adsorbed CO were totally absent thus indicating that the bands observed in the spectra of CO adsorbed on 1%Rh-LaCoO₃/ Al_2O_3 catalyst are associable to the noble metal only.

DRIFT spectra of CO adsorbed on 1%Rh-LaCoO₃/ Al_2O_3 catalyst as reduced and after a short (15 min) and long (120 min) exposure respectively to a 20 ppm H_2S /2% H_2 / N_2 mixture (chosen to simulate S-poisoning under reducing condition typical of tar conversion tests) are shown in Fig. 5. The dominant features of the DRIFT spectrum of CO adsorbed over the reduced catalyst are the doublet bands at 2090 and 2016 cm^{-1} corresponding to gem-dicarbonyl

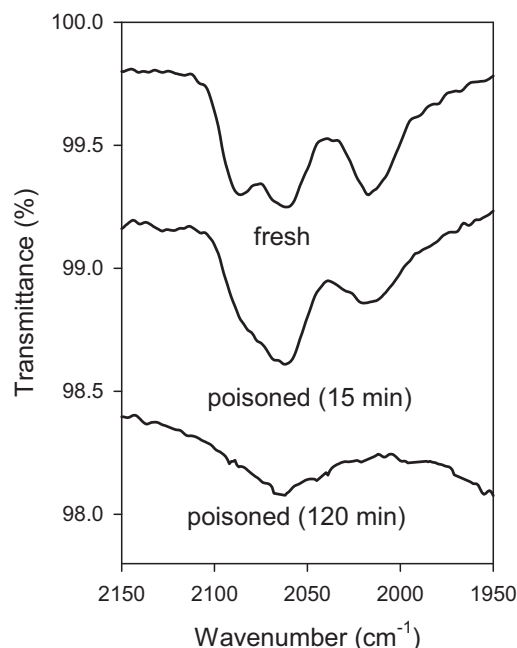


Fig. 5. DRIFT spectra of CO adsorbed at room temperature on fresh and poisoned 1%Rh-LaCoO₃/ Al_2O_3 .

species on isolated Rh sites and a band at 2060 cm^{-1} assigned to the linearly adsorbed CO on Rh crystallites or clusters in the zero oxidation state [21]. The short sulphur exposure results in the reduction of the bands associated to isolated Rh sites which completely disappear upon a long exposure. This result is in agreement with Cimino et al. [22] who observed for Rh/ Al_2O_3 catalyst a selective poisoning of highly dispersed Rh sites whereas larger noble metal crystallites are not modified by sulphur. Therefore, it shows that alumina and perovskite have qualitatively the same effect. This results is also in agreement with the higher fraction of dispersed rhodium [23] present in the 0.5%Rh-LaCoO₃/ Al_2O_3 sample which shows a slight decrease of reforming products balanced by an increase of CO_2 and methane in the gas produced by tar conversion upon addition of 20 ppm H_2S . The apparent discrepancy with the saturation time of catalytic tests is probably related to the much higher contact time carried out in the DRIFT cell compared to that of the fixed bed reactor used for catalytic tests.

In Fig. 6 H_2 TPR signals of fresh and poisoned catalysts are compared. TPR curve of the sulphur poisoned La-doped alumina used as support is also reported. It should be pointed out that the H_2 uptake is associable to the reaction with metal oxide species only for fresh samples whereas it can be attributable to the reaction both with the oxides and with sulphide, sulphite and sulphate species for poisoned catalysts. All poisoned catalysts show TPR profiles different from those of the fresh samples confirming that different species are formed upon poisoning.

The profile of the fresh 1%Rh/ Al_2O_3 shows the typical peaks ascribable to dispersed rhodium oxide and rhodium aluminate at low and high temperature respectively [3]. Poisoning of this sample results in the appearance of a well defined signal at very low temperature (about 130 °C) whereas the intermediate peak starts about 80 °C before, in addition, a large peak overlaps that at high temperature.

The presence of a peak at low temperature was also found by Cimino et al. [12] for a Rh/ Al_2O_3 sample treated with SO_2 under oxidizing conditions and was attributed to the reduction of $Rh_2(SO_4)_3$ species. In fact, it is reported [24] that SO_2 can be oxidized to SO_3 over noble metals and sulphates formation can then take place. Although O_2 was not fed in the catalyst treatment, we can suppose

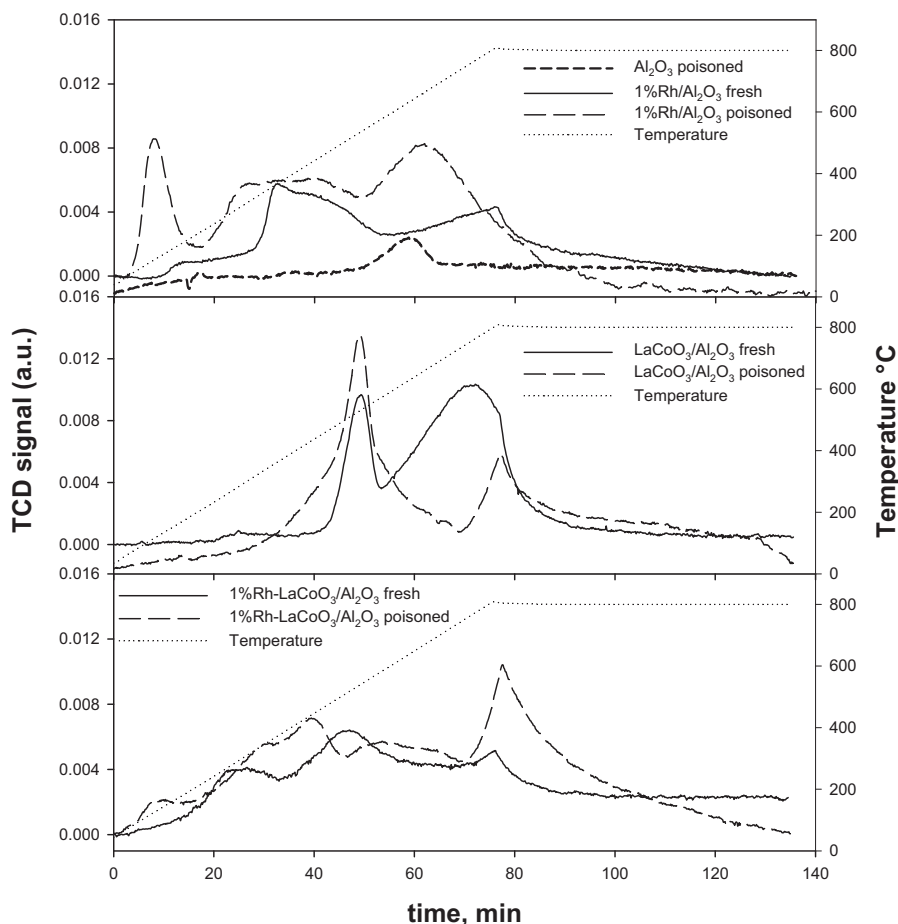


Fig. 6. H_2 TPR profiles. TCD signals of fresh and poisoned catalysts and temperature profiles as functions of time.

that the oxygen of the metal oxide can be involved in this reaction. On the other hand, formation of rhodium sulphide can also occur since formation of noble metal sulphides is favoured high H_2S partial pressure [19] and a possible contribution in the middle temperature region cannot be excluded. Finally, the peak at high temperature can be associated to the reduction of aluminum sulphate. In fact the same peak was observed for the pure support even if with a lower intensity. The intensity increases in the presence of the noble metal because rhodium oxide promotes the formation of SO_3 which spills over to the support [24]. This peak is lower than that detected by Cimino et al. [12] for the same catalyst likely due to the limited oxygen availability of the present experiment. In conclusion, although the presence of different sulphur species is predictable for this sample, in agreement with the catalytic activity results, a large fraction of rhodium oxide, considered active for the reforming reaction, is still present thus only slightly affecting the good properties of this catalyst.

The fresh LaCoO_3 shows a TPR profile typical of the supported perovskite with a peak at lower temperature assigned to the reduction of cobalt from +3 to +2 and an additional peak at higher temperature related to the reduction of Co^{2+} to Co^0 .

Sulphur poisoning changes the TPR profile increasing the low temperature peak and strongly decreasing that at high temperature. It is reported for $\text{LaCoO}_3/\text{Al}_2\text{O}_3$ that under oxidizing conditions SO_2 poisoning causes the destruction of the structure with the formation of $\text{La}_2(\text{SO}_4)_3$, $\text{La}_2(\text{SO}_3)_3$, $\text{La}_2\text{O}_2\text{SO}_4$ and CoO [17]. The formation of sulphates and sulphites of lanthanum and of simple oxides of B metal were also supposed by Zhang et al. [25] carrying out TPR of sulphated $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$. Moreover, under reducing

conditions the formation of bulk cobalt sulphide is favoured even at low sulphur partial pressure with respect to that of noble metals sulphide [19]. Therefore, due to the decrease of the peak associated to the reduction of Co^{2+} it is more probable to suppose that CoS is formed which can contribute to the increase of the low temperature peak. Therefore, the loss of perovskite structure, together with the formation of CoS , can explain the reduced activity of this catalyst in the presence of H_2S , even at low concentration.

The dispersion of rhodium on the perovskite layer (fresh $1\%\text{Rh-LaCoO}_3/\text{Al}_2\text{O}_3$) causes a partial destruction of the perovskite structure also ascribable to the double calcination the sample underwent, which promotes migration of cobalt into the alumina lattice thus affecting its reducibility. The peak associated to rhodium oxide is still detectable although at a temperature lower than the $1\%\text{Rh}/\text{Al}_2\text{O}_3$ thanks to the barrier effect of perovskite [3].

The S-poisoned sample shows a peak at very low temperature, similar to that attributed to rhodium sulphate for $1\%\text{Rh}/\text{Al}_2\text{O}_3$ sample, and the appearance of some additional signals overlapping those present in the fresh sample. In the temperature range 200–600 °C at least three peaks can be detected, which can be associated to Rh and Co sulphide in addition to Rh oxide. Although the attribution of a so high number of superimposed peaks is quite complex, we can assert that a lower amount of rhodium sulphate with respect to the sample not containing the perovskite was detected suggesting that perovskite preserves more than alumina rhodium from sulphate formation probably keeping a higher amount of rhodium oxide available for the reaction.

4. Conclusion

The effect of the presence of H₂S on the performance of a very active Rh–LaCoO₃/Al₂O₃ catalyst in biomass tar conversion was evaluated.

Results showed that the perovskite layer preserves to large extent Rh from poisoning. When saturation limits are overcome highly dispersed rhodium, associated to the reforming centres, is mainly affected and, as a consequence, the formation of reforming products decreases balanced by the production of total oxidation and cracking species, as CO₂ and light hydrocarbons respectively. The perovskite layer has a higher adsorption capacity with respect to the La-doped alumina used as support providing a greater sulphur tolerance to the catalyst containing rhodium dispersed in the LaCoO₃ matrix. This catalyst keeps its original reforming properties showed for S-free feed also in the presence of high sulphur concentration.

The preservation from sulphur poisoning of dispersed rhodium oxide, active in tar reforming, was confirmed by DRIFT and TPR experiments.

Acknowledgement

The authors thank Mr. Vitale Stanzione for his assistance in chromatographic analysis. This work was financially supported by “CO₂ capture – Carbone pulito” project (MiSE).

References

- [1] M. Ni, D.Y.C. Leung, M.K.H. Leung, K. Sumathy, *Fuel Process. Technol.* 87 (2006) 461–472.
- [2] J. Gil, J. Corella, M.-P. Aznar, M.A. Caballero, *Biomass Bioenergy* 17 (1999) 389–403.
- [3] P. Ammendola, L. Lisi, B. Piriou, G. Ruoppolo, *Chem. Eng. J.* 154 (2009) 361–368.
- [4] P. Ammendola, B. Piriou, L. Lisi, G. Ruoppolo, R. Chirone, G. Russo, *Exp. Therm. Fluid Sci.* 34 (2010) 269–274.
- [5] I. Obernberger, T. Brunner, G. Bärnthaler, *Biomass Bioenergy* 30 (2006) 973–982.
- [6] L. Li, C. Howard, D.L. King, M. Gerber, R. Dagle, D. Stevens, *Ind. Eng. Chem. Res.* 49 (2010) 10144–10148.
- [7] J. Hepola, P. Simell, *Appl. Catal. B: Environ.* 14 (1997) 287–303.
- [8] H. Rönkkönen, P. Simell, M. Reinikainen, O. Krause, *Top. Catal.* 52 (2009) 1070–1078.
- [9] K. Sato, K. Fujimoto, *Catal. Commun.* 8 (2007) 1697–1701.
- [10] K. Tomishige, M. Asadullah, K. Kunimori, *Catal. Today* 89 (2004) 389–403.
- [11] S. Cimino, R. Torbati, L. Lisi, G. Russo, *Appl. Catal. A: Gen.* 360 (2009) 43–49.
- [12] R. Torbati, S. Cimino, L. Lisi, G. Russo, *Catal. Lett.* 127 (2009) 260–269.
- [13] I. Rossetti, O. Buchneva, C. Biffi, R. Rizza, *Appl. Catal. B: Environ.* 89 (2009) 383–390.
- [14] S. Specchia, A. Civera, G. Saracco, V. Specchia, *Catal. Today* 117 (2006) 427–432.
- [15] M. Alifanti, R. Auer, J. Kirchnerova, F. Thyron, P. Grange, B. Delmon, *Appl. Catal. B: Environ.* 41 (2003) 71–81.
- [16] I. Rosso, G. Saracco, V. Specchia, E. Garrone, *Appl. Catal. B: Environ.* 40 (2003) 195–205.
- [17] Y. Zhu, R. Tan, J. Feng, S. Ji, L. Cao, *Appl. Catal. A: Gen.* 209 (2001) 71–77.
- [18] CEN/TS 15439, Technical specification: biomass gasification-tar and particles in produced gas-sampling and analysis, European Committee for Standardization, 2006.
- [19] M.V. Mundschaue, C.G. Burk, D.A. Gribble Jr., *Catal. Today* 136 (2008) 190–205.
- [20] M. Ferrandon, J. Mawdsley, T. Krause, *Appl. Catal. A: Gen.* 342 (2008) 69–77.
- [21] E. Finocchio, G. Busca, P. Forzatti, G. Groppi, A. Beretta, *Langmuir* 23 (2007) 10419.
- [22] S. Cimino, L. Lisi, G. Russo, R. Torbati, *Catal. Today* 154 (2010) 283–292.
- [23] P. Ammendola, R. Chirone, L. Lisi, B. Piriou, G. Russo, *Appl. Catal. A: Gen.* 385 (2010) 123–1123.
- [24] T. Wang, A. Vazquez, A. Kato, L.D. Schmidt, *J. Catal.* 78 (1982) 306–318.
- [25] R. Zhang, H. Alamdari, S. Kaliaguine, *Appl. Catal. A: Gen.* 340 (2008) 140–151.